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RESEARCH HYDROXYAPATITE CRYSTALS AND ORGANIC COMPONENTS OF HARD TOOTH TISSUES AFFECTED BY DENTAL CARIES USING FTIR-MICROSPECTROSCOPY AND XRD-MICRODIFFRACTION

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Abstract. Investigations of the intact dental enamel as well as carious-affected human dental enamel were performed in the work with the use of IR-spectromicroscopy and X-ray diffraction applying synchrotron radiation. Caries of enamel was shown to be characterized by an increase of the number of deformation and valence vibrations for N-C-O, N-H and C=O bounds, decrease of crystallinity index and by the absence of the preferable orientation of hydroxyapatite (HAP) crystals within the affected enamel. It indicates the presence of the destructive processes in the organic matrix of hard tooth tissues.

Keywords: hydroxyapatite, human dental enamel; caries; synchrotron radiation; XRD; FTIR.

INTRODUCTION

Biological composites are currently of a great interest for many research groups involved to the study of their properties, structure and functioning, attracting all kinds of modern methods of physical and chemical analysis of materials to it [1, 2]. A characteristic feature of biological composites is on the one hand their small size and on the other — versatility, due to a complicated hierarchy of their structure. Based on the analysis of scientific articles it can be argued that enamel and dentin of human teeth should be the focus of research into biological composites. This is not surprising, given that dental caries is a major problem in modern dentistry and one of the main research fields of the science. According to many researchers, resistance to dental caries is related to the structure and properties of hard tissues of the tooth.

Dental enamel is known to be the hardest human tissue. This allows it to withstand the impact of large mechanical loads while the tooth is performing its functions. It is well known that enamel consists by more than 90% of the mineral compounds (mainly hydroxyapatite — HAP [$Ca_{10}(PO_4)_6(OH)_2$], fluorapatitea [$Ca_{10}(PO_4)_6F_2$], carbonated apatite et al.), by 1,2% — of organic compounds and referred to the bound water in the crystals and organic components as well as free water [3].

The data on the organic compounds contained in the mature enamel is rather provisional. G. Jenkins [4] presented the following numerical data on the content of organic compounds in the enamel of pre-molars and molars (% of dry solid matter): insoluble proteins — 0,3—0,4%, soluble proteins — 0,05%, fats — 0,6%, citrates — 0,1%. The most wide-spread proteins (about 90% of all the organic fraction) are hydrophobic proteins (amelogenins), enriched with amino acids and detected mainly in the immature enamel, characterized by a high concentration of proline, glutamic acid, leucine and histidine, 10% — are acidic proteins — enamelins, determined in a completely mature enamel, arranged in the interprism substance with a high molecular mass and characterized by a high concentration of aspartic and glutamic acid, serine and glycine [5].

Hard dental enamel is known to be in a state of permanent demineralization and remineralization; if the first kind of processes dominates over the second one, caries may appear. The development of the caries

process is accompanied by the formation of several different areas in the enamel: translucent zone, dark zone, caries core and superficial zone. For different stages of the development of the caries process, especially pigmented spot the content of protein within the lesion shows a third or fourth-fold increase and this spot can not transform into a carious cavity for several years, however, a considerable decrease in calcium and phosphorus is observed in this area, which is called demineralization. Prior to the appearance of the cavity within the hard dental tissue, the development of caries process is reversible and the structure of enamel can be recovered. Probably, just protein plays an important role in the processes of stabilization and reversibility of the processes of focal demineralization in hard dental tissues [6].

Organic matrix bound to the crystals and providing their growth and orientation during formation of the enamel is almost completely lost during maturation of dental enamel. It is preserved in the form of the finest 3D protein grid while its wires are arranged between the prisms. Recent investigations provided new data on the nature and functions of an organic matrix of the enamel. It was confirmed that its most important role is the stabilization of the buffer system providing the presence of the free calcium ions in this system [7]. It should be noted that organic components of the enamel matrix has been so far studied to a less extent that its mineral phase. Calcium-binding protein which is capable of depositing in the neutral medium in the presence of calcium ions is considered as the functional elementary block of the organic matrix in the enamel. Calcium-binding protein of the enamel and acid-insoluble protein both determine orientation of the crystals in enamel prisms and its structure. Significance of the protein for enamel has not been studied yet and a lot of scientists consider that it plays only a passive role in the enamel formation. However, there is a view that resistance to caries for the enamel depends not only on the content of inorganic components, but also on the amount of protein. "Protein grid" surrounding apatites of enamel prevents the contact of an acid with the apatite and also dampens its effect. Thus, the understanding of the processes taking place in the enamel both in its normal state as well as in the pathology condition is largely dependent on the knowledge of its constituents as well as on the connection between organic matrix and inorganic substance.

A number of investigations of the human teeth were previously performed, including studies into synchrotron radiation.

So, in the article [8] the early caries lesion in bovine tooth enamel was studied by two different X-ray diffraction systems at the SPring-8 third generation synchrotron radiation facility. The simultaneous small- and wide-angle measurement with a microbeam is a powerful tool to elucidate the mechanisms of demineralization and remineralization in the early caries lesion.

The usefulness of integrated FTIR and XRD studies in evaluation of carbonated hydroxyapatite powders has been confirmed in the work [9].

As was shown in [10], microstructural studies of dental hard tissue can be performed using Raman microspectroscopy. It was concluded that microspectroscopy provides a cutting-edge high-resolution and non-destructive method for exploring the role of microstructure on the residual stress distribution within natural biocomposites.

However, only hard dental tissues were mainly studied predominantly in the powder-like form in the works [6, 11—12], which is really convenient for investigations with the use of powder diffraction technique, but in this case experiments can not be considered as pure ones.

Therefore, the study of the structure and chemical composition of the intact and caries-affected dental enamel will give a more profound understanding of original changes in the hard dental tissues. Since the surface of enamel at the initial stages of caries process is relatively small, the most convenient and useful method to carry out this kind of study will be microdiffraction of the X-rays which provides valuable and detailed data on the mineral content of as intact as caries-affected teeth. As for the study of organic substances of enamel, it seems reasonable to apply IR-Fourrier spectromicroscopy that allows one to reveal the presence of organic (protein) components (protein ones) in the enamel.

OBJECTS AND METHODS OF INVESTIGATIONS

A sample of the tooth with caries lesion extracted from a patient according to orthodontic indications in a case of severe paradontosis was prepared as follows. First, the tooth was washed up in flowing water, removed dental deposit, after that its surface was dried with filter paper. Next the tooth was sawed up at a specialized device using a diamond disk under water cooling and as a result a plate was obtained with a the thickness of up to 1 mm. The prepared slice was stuck onto a glass plate with a the thickness of 2 mm using acrylic glue and then it was grinded and further polished applying diamond paste. Fig. 1a represents the photo of the analyzed sample.

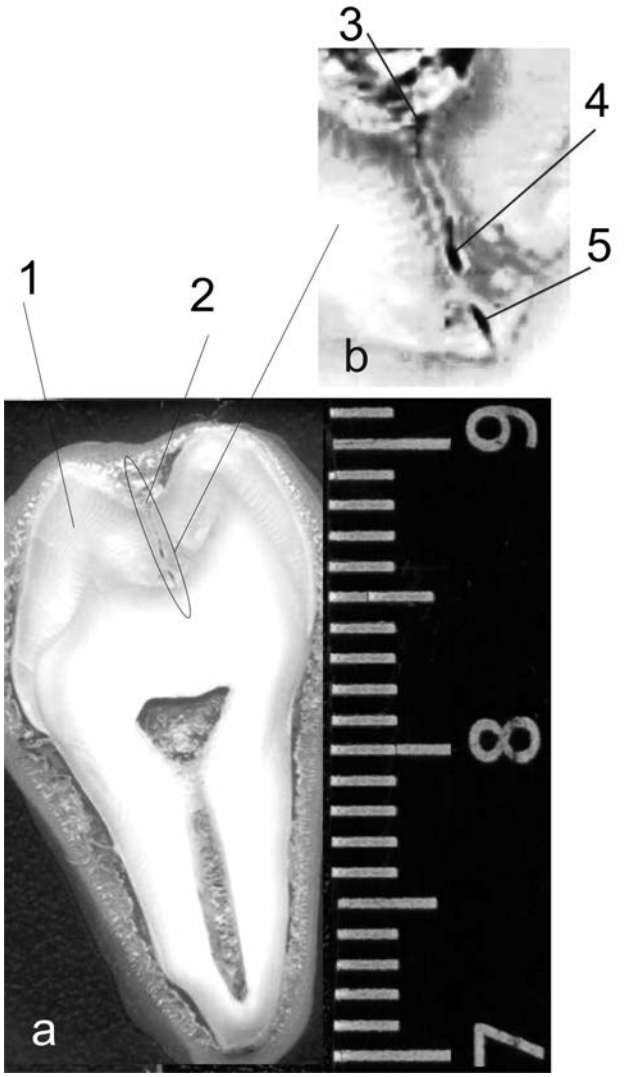

Fig. 1. Frontal slice of the tooth where the investigated areas are indicated. (Right scale in centimeters). a) Total view of the tooth b) the fissure carious canal. 1—5 are the points that were used for the study

At first we made the investigations at the Infrared Spectromicroscopy beamline of synchrotron SRC Aladdin, University of Madison, State of Wisconsin, USA, that operated within the range of 720 to 4000 cm^{-1}, with the use of Fourier spectrometer Thermo Fisher Scientific aligned with IR microscope. The size of a spot (horizontal x vertical) is 25 mm x 12 mm.

The area of the analyzed sample surface during a survey of IR-spectra with the use of microscope was 20 x 20 mm^2. The study of microstructure of the dental tissue by X-ray microdiffraction was performed at ANKA-PDIFF beamline of ANKA synchrotron, Karlsruhe, Germany. The radiation source was 1.5T swivel magnet arranged at a synchrotron ring (E c = 6keV). Monochromatic emission corresponding to copper $K\alpha_1$ radiation with a wavelength of λ=1.54032Å was used in the experiments. Flux at sample position ≈2x1010 ph/s/mm^2 at 10 keV, based on 100 mA beam current and 0.1% bandwidth. Beam size at sample ≈0.5 mm (H) x.5 mm (V) (focused). In this case the analyzed area was 100x100 mm.

The points 1 and 2 of the figure 1 were used for obtaining of IR-reflection spectra, while the points 3—5 in the carious canal which are presented in the fragment 1, b were used for the microdiffraction study.

FTIR-spectromicroscopy

Application of IR-microscopes operating in the reflection mode as well as a high intensity of synchrotron radiation as a source of IR-emission allowed the scientists to make a rather successful analysis of the state of dental tissue by obtaining information from a small part of the polished surface [12] which is in fact an even flat surface. Using Kramers-Kronig relations, we have recalculated IR-reflection spectra obtained in the experiment involving IR-absorption spectra since in a number of works dealing with the analysis of IR-spectra for dental enamel IR-absorption spectra are usually presented [13—15]. Spectral range from 2000 to 900 cm^{-1} was selected for the detailed analysis since only in this region the main features determining the nature of dental enamel can be observed. The obtained results are presented in Fig. 2.

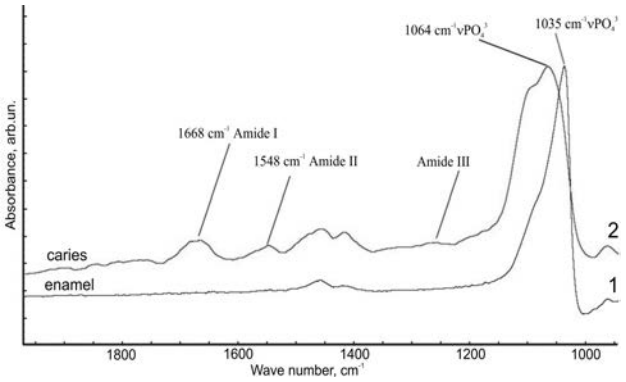

Fig. 2. IR-absorption spectra (1 — intact enamel, 2 — carious enamel)

As is seen from this figure, IR-absorption spectra obtained from the investigated sample involve absorption bands characteristic of the dental enamel. Absorption spectrum obtained from the part of healthy (intact) enamel (1) considerably differs from that of the part of enamel affected by caries (2). In this spectral range the main absorption band related to the stretching vibrations νPO_4^3 in the spectrum (1) has its peak at 1035 cm^{-1}; it is rather narrow and has weakly expressed

"shoulder" in the short wavelength side. Two weak peaks besides this band can be quite easily seen at 1415 cm^{-1} and at 1450 cm^{-1} corresponding to the plane asymmetrical deformational vibrations δ as (CH_3). The bands of secondary amides — Amide I (υ (C=O) 1661.7—1664.2 cm^{-1}), Amid II (δ (C-N) 1555.8 cm^{-1}) (mixed stretching-deformational vibrations of N-H and C-N bonds), Amid III (δ (NH) 1240.4 cm^{-1}) can be observed in the spectra of enamel affected by caries in addition to the bands related to inorganic constituents of the tooth. Since the observed absorption bands are connected with the presence of amino acids in the dental tissue, and the chains of these acids form protein, the value of their integral intensity makes it possible to make a conclusion on the protein concentration. A quantitative characteristic of the relative concentration for the protein component in the dental tissue can be the ratio of the integral intensity of Amide I, Amide II and Amide III absorption bands to the value of the integral intensity of ν (PO_4^{-3}) band, that characterizes mineral (inorganic) component of the dental tissue. Calculations of this ratio were made with the use of spectral software system OMNIC. The obtained data is presented for clearness in the form of histograms in Fig. 3, a and 3, b.

Comparing the results of experimental investigations, we found a good coincidence of the absorption peaks positions with each other. It means that the obtained results are rather correct and they allow one to follow some specific regularities. For example, absorp-

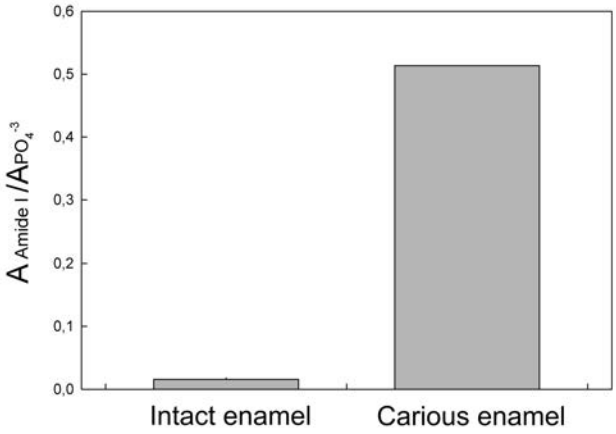

Fig. 3 a. Histogram $A_{AmideI} / A_{PO4}^{-3}$

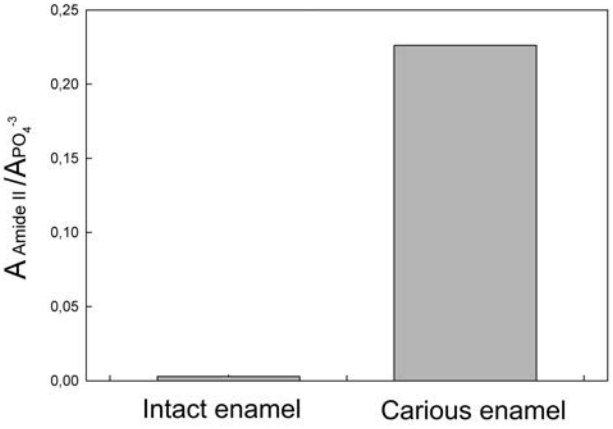

Fig. 3 b. Histogram $A_{AmideII} / A_{PO4}^{-3}$

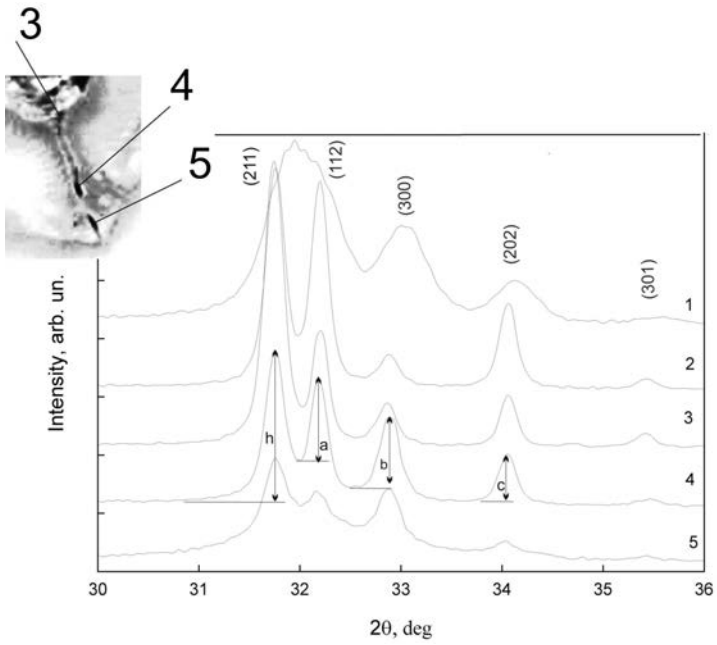

Fig. 4. The results for X-ray microdiffraction. 1 — Synthesised bio HAP [16]; 2 — Sound enamel (point 1, fig.1); 3—5 correspond to the points 3—5 in the carious canal are presented in the fragment 1, b were used for the microdiffraction study

tion bands related to the protein component (Amide I, Amide II) in all of the spectra are considerably smaller than those related to the mineral (inorganic) component. It can be clearly observed in the spectra as well as in the histograms. At the same time the areas of enamel affected by caries or those arranged in their vicinity are characterized by the highest content of organic component and the ratio of the component related with Amide I to that one connected with Amide II is approximately 2 : 1.

X-ray microdiffraction

The results of X-ray microdiffraction for the investigated samples obtained in the range of angles of the most intensive lines in the spectrum of synthesized microcrystalline bioactive hydroxyapatite — (1), intact enamel — (2) and three points of caries proliferation with an increase in the depth: — (3) the beginning of fissure, (4) — the center of fissure, (5) — the bottom of fissure, respectively, are presented in Fig. 4.

The obtained experimental data suggests that Miller indices for the investigated materials correspond to synthetic Calcium Phosphate Hydroxide (Hydroxylapatite) $Ca_{9.868}$ (PO_4) $_{5.586}$ (OH) $_{4.006}$ HAP. No any additional phases on the basis of calcium are present in the samples.

Using Rietveld method, we calculated parameters of the crystalline lattice for the analyzed areas of tooth. The data is presented in Table 1.

Table 1. The results of XRD-microdiffraction analysis

		Cell parameters		Texture index		Crystallinity index, CI	HAP crystal size, nm ±5 nm
		a, Å ±0.01 Å	c, Å ±0.01 Å	R (300)	R (112)		
Synthesised bio HAP [16—18]		9.40	6.87	-	-	-	40
Sound enamel (Point 1, fig.1)		9.44	6.88	11.3	2.1	1.1	40
carious-affected enamel (fig.1)	Point 3	9.44 (5)	6.88	10.6	4.7	0.5	35
	Point 4			3.16	2.6	1.3	40
	Point 5			2.35	2.9	0.6	30

As is seen from Fig. 4, hydroxyapatite crystallites in the different analyzed regions of the human dental enamel are characterized by a clearly defined preferable orientation that can be observed by the change of intensities for three most strong lines (211), (300), (112) in the X-ray diffraction patterns of the samples.

In order to make some quantitative estimations of the texture degree, one can use the value called texture index of a sample — R which can be determined by the ratio of intensities for the most strong lines I (211) /I (300) and I (211) /I (112) [11]. For the reference sample of hydroxyapatite in the powder form the ratio of intensities for the most strong lines in the diffraction spectrum is as follows I (211) /I (300) =1.63 and I (211) /I (112) =1.94.

Therefore, texture index can be calculated in the following way

$$R(300) = I(211) / I(300) / 1.63$$

$$R(112) = I(211) / I(112) / 1.94$$

If R=1, then crystallites of hydroxyapatite are distributed randomly, while R>1 or R<1 indicates at a preferable orientation of HAP crystals in the enamel and it means formation of the texture. Our calculations show that texture index R (300) for intact enamel is equal to 11.3 while for the points (3) — (5) in fissure canal it is 10.6, 3.16, 2.35 respectively (See Table 1).

In order to examine the changes in the structure of hard dental tissues during the development of carious process in the tooth, we can provide semi-quantitative estimations of these changes by analyzing the results of X-ray diffraction presented in Fig. 4 by introducing a crystallinity index proposed by Pearson et al [19]. According to this method, crystallinity index for hydroxyapatite crystals can be calculated with the use of diffraction peaks height h = (211), a= (112), b = (300) and c = (202). The main problem of the proposed technique lies in the correct separation of these peaks in the diffraction pattern. The height of the peak is measured as presented in Fig. 4 for diffraction from the area inside

a carious fissure: from maximum of the diffraction line to the minimum of the line intensity — hollow formed by two close lines (see Fig. 4). Thus, crystallinity index can be determined according to the following expression

$$CI = \frac{a+b+c}{h}$$

The calculated crystallinity index CI for the intact enamel takes the following value of 1.11, that coincides with that presented in [20], while for the points (3) — (5) in the carious fissure this index takes the values of 0.55, 1.28 and 0.62 respectively (See Table 1).

It is known that content of the ordered or, in other words, crystalline part of matter in the samples is proportional to the crystallinity index. So a decrease in the index means amorphization of HAP crystal. The obtained results allow one to make a conclusion that with an increase in the carious cavity size — in our case this is caries of dental enamel fissure — HAP crystals that are ordered in intact enamel along the direction perpendicular to dentine-enamel junction are randomly distributed with the depth of carious process in collagen matrix — protein network. This case corresponds to microcrystalline powder HAP. At the same time amorphization of hydroxyapatite crystal itself can be observed, which indicates its destruction.

Based on the experimental data, we can determine the size of hydroxyapatite crystals according to Scherer formula:

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where D — is a size of crystallites, K — is a constant close to 0.9, l — is a wavelength of characteristic radiation for copper 1.540598Å, b is a half-width of X-ray line (211) used for the analysis, q is Bragg angle for (211) a crystal plane. The obtained results are presented in Table 1 HAP crystal size for intact enamel is of ~ 40 nm; one can note that this size is reduced as under moving into fissure.

It should be noted that in [20] similar investigations of the hard dental tissues by X-ray microdiffraction are discussed; however, the size of HAP crystallites determined by the authors of the work considerably differs from that calculated in our studies. Probably, while determining the size of HAP crystallites in the enamel and dentine the authors of [20] made a mistake. It can be due to a low angle resolution of the plane X-ray detector used for obtaining of Debye patterns. Diffraction planes (211) and (112) merged into a common diffraction peak (it can be easily seen form the plots presented in [20]) and the half-width of this peak was just used for the calculations of HAP crystal size.

Using the inverse calculation involving the Scherrer equation for determining the amount of hydroxyapatite crystals and the data of Xue et al. about the size of HAP crystals, we can determine the half-width of the diffraction lines used for the calculation. By comparing the calculated value of the diffraction peak half-width and experimental half-width of a picture in the paper [20], it can be seen that Xue et al. for its calculation erroneously used unresolved diffraction peak of (211) and (112) reflections, while needed to use a diffraction plane (211).

That is why it is so important to apply high-precision goniometer and detector with a high space resolution while analyzing low-symmetry crystal systems.

RESULTS

The results presented above clearly demonstrate the difference between intact enamel and enamel under emerging carious fissure. A greater size of a crystal (40 nm), high texture and crystallinity indices as well as minimum of organics content — all this characterizes intact enamel and agrees with the up-to-date concepts on the structure of enamel and results of the works similar to our research [6, 11, 19, 20]. At the same time emerging of fissure caries is characterized by an increase in organics content in fissure canal according to the data of IR-spectromicroscopy [21, 22]. The analysis of the different points in fissure canal by X-ray microdiffraction showed a decrease in the sizes of HAP crystallites with the depth that can be due to specific features in the dental structure but also it may be the result of the carious process connected with diminishing crystallinity and texture indices.

CONCLUSIONS

Therefore, fissure caries of enamel is characterized by an increase in the number of deformation and stretching vibrations of N-C-O, N-H and C=O bonds, decrease in crystallinity and texture indices as well as by the absence of the predominant orientation of HAP crystals in the affected enamel; it means destructive disease in an organic matrix of hard tooth tissues. Due to subsurface demineralization, dental enamel crystals themselves are further destroyed.

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